

Glycol Glycosides in Alkyds

W. J. MCKILLIP, J. N. KELLEN,* C. N. IMPOLA, R. W. BUCKNEY
Ashland Chemical Company†

And

F. H. OTEY
Northern Regional Research Laboratory
United States Department of Agriculture**

Glycol glycosides derived from starch were successfully prepared in pilot-scale quantities and were demonstrated to have properties and a production cost acceptable for use in both conventional and urethane alkyds. Procedures were developed for incorporating the glycosides into four major classes of alkyds. These alkyds were evaluated in both clear and pigmented films and shown to have superior drying and hardness, equivalent flexibility, but slightly inferior gloss and yellowing characteristics when compared with industrial controls based on pentaerythritol-glycerol polyols.

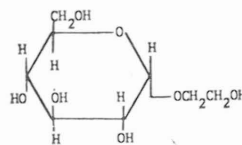
INTRODUCTION

Generally, alkyd resins are prepared by reacting triglycerides or fatty acids with polyhydric alcohols (polyols) followed by cross-linking with dibasic anhydrides. Variation in these components and the amounts used give innumerable varieties of alkyd resins. Closely related to these conventional resins are the urethane alkyds, which are obtained by substituting diisocyanates for part or all of the dibasic anhydride.

Since more than one-half billion pounds of alkyds are produced annually,¹ a search continues for new raw materials that will either improve the properties or reduce the cost of alkyd resins. This paper describes the successful use of glycol glycosides as part of the

polyol portion of alkyds. At present, glycerol and pentaerythritol are among the predominant polyol components used in commercial alkyds. These industrial polyols are usually quoted at about 25 cents/pound. In contrast, we found that glycol glycosides can have a selling price of about 12 cents/pound. Consequently, the economics of using glycol glycosides in alkyds appear favorable.

Glycol glycosides are obtained by reacting ethylene glycol with starch. They are a mixture containing 45% glycol α -D-glucoside, 21% glycol β -D-glucoside and 34% mixed glycosides with two or more glucose units per glycol unit.² Glycol glycosides can best be represented by the structure shown below for glycol α -D-glucoside.



This idealized structure has five hydroxyls available for esterification, two primary and three secondary. However, when allowance is made for the mixed glycosides, the products have an average of 4.6 hydroxyls and an average formula weight of 212/glucose unit.

GLYCOL GLYCOSIDE PREPARATION

The manufacture of glycol glycosides is simple and involves transglycosylation of corn starch with ethylene glycol. The "gel" procedure previously reported^{3,4} consists of heating a slurry of corn starch, ethylene glycol, and sulfuric acid catalyst at 120 to 145 C until a liquid product is formed. During the early stages of the reaction, a heavy gel makes stirring difficult. On continued heating, the gel breaks and the

A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract was supervised by the Northern Utilization Research and Development Division of the Agricultural Research Service. Mention of names of equipment or specific industrial products does not constitute endorsement by the U. S. Department of Agriculture over similar equipment or products not mentioned.

* Present address: Iowa State University, Iowa City, Iowa.

† 10701 Lyndale Ave. S., Minneapolis, Minn. 55420.

** This is a laboratory of the Northern Utilization Research and Development Division, Peoria, Ill. 61604.

Table 1—Estimated Production Cost Per Pound
Of 70% Glycol Glycoside

Item	FIXED CAPITAL INVESTMENT	
	\$238,000	\$298,000
	GLYCOL GLYCOSIDE COST,	
	Cents/lb., 70% Solution	
Raw materials ^a	6.170	6.170
Labor, direct	0.364	0.364
Labor, burden	0.055	0.055
Supervision	0.090	0.090
Plant overhead	0.218	0.218
Utilities	0.097	0.097
Maintenance, taxes, insurance	0.238	0.298
Depreciation	0.238	0.298
Total plant gate cost	7.470	7.590

(a) Based on following commercial prices (per lb.): ethylene glycol, 11.5 cents; starch, 5 cents; sulfuric acid, 1.7 cents; calcium carbonate, 5.7 cents; carbon, 39.5 cents, and filter aid, 6.5 cents.

viscosity rapidly reduces to a constant value of 2000 ± 500 cps.

To overcome the gel problem in scale-up studies, Leitheiser, *et al.*⁵ devised a "reverse" procedure for preparing glycol glycosides. Gelation is avoided in the improved procedure by adding corn starch slowly with agitation to the ethylene glycol and sulfuric acid previously heated to 120 to 130 C.

Pilot-Scale Procedure

Glycol glycosides used in this investigation were prepared in the pilot plant by the following reverse procedure: Charge a 30-gallon stainless-steel reactor with 133 pounds of ethylene glycol and 0.64 pound of sulfuric acid and heat to 120 C with good stirring and a nitrogen blanket. Add 100 pounds (87 pounds, dry basis) of Pearl corn starch over a 40-minute period while maintaining a temperature of 120 C. When addition is complete, reduce the pressure to 40 mm Hg and continue heating and stirring for 30 minutes. Then cool the mixture and neutralize the sulfuric acid with 0.65 pound of calcium carbonate. Again seal the reactor and remove the unreacted ethylene glycol at 5 to 10 mm Hg as the temperature is slowly raised to about 140 C. After stripping is complete, dissolve the glycoside in 100 pounds of water, decolorize with 5 pounds of charcoal, filter, and finally, adjust the concentration to 70 to 80% solids in water.

Glycol glycosides prepared as described above are clear, odorless, and have a color of Gardner 1. Approximately 0.8 mole of glycol react per anhydroglucose unit to give a calculated hydroxyl equivalent weight of 46. Further details on their properties have been published.⁶

Economics

Because glycol glycosides show industrial potential, their production cost was investigated. These preliminary studies revealed that a plant investment of \$238,000 (−20%, +35%) is necessary to produce 10 million pounds/year of 70% glycol glycoside in water.

Using the plant investment at nominal and at +25%, the plant gate cost per pound of 70% glycol glycoside is shown in Table 1, with a depreciating straight line over 10 years. These plant gate costs of 7.47 and 7.59 cents/pound can be raised to 8.44 and 8.56 cents when approximate costs for sales, administration, and research are considered together with profit necessary to return 30% on investment before federal taxes. On the basis of 100% solids, the selling price of glycol glycosides would be 12.06 and 12.33 cents/pound.

ALKYD RESIN PREPARATION AND EVALUATION

Four major classes of alkyds were prepared and evaluated: (1) long, (2) medium, and (3) short oil length, and (4) urethane alkyds. The amount of oil present in the finished alkyd determines its classification as a short (20-45% oil), medium (46-56% oil), or long (58-80% oil) oil length resin. Urethane alkyds were made by substituting toluene diisocyanate for the dibasic anhydrides used in conventional alkyds.

Optimum reaction conditions and formulations were established for processing glycol glycoside-based alkyds. In general, the processing techniques conventionally used in alkyd synthesis are applicable to preparing glycol glycoside-based alkyds. Xylene azeotropic distillation of the water provided superior products to those from the fusion cook method. The xylene gave much better reaction control and, consequently, improved resin color. Furthermore, since it was advantageous to add the glycol glycosides as a 70 to 80% solids in water solution, the azeotropic distillation procedure allowed easy removal of the water.

The hydroxyls in glycol glycosides that are available for esterification are less than the analyzed 4.6 because of internal anhydridization at alkyd processing temperatures. Steric hindrance, due to this internal ether formation, makes it difficult to obtain low acid number products when using glycol glycosides as the sole polyol. For this reason we formulated alkyds using a copolyol with glycol glycosides. The additional polyol, glycerol, also aids in solubilizing the glycosides and prevents minor char formation. Poor color products resulted when glycol glycosides were used as the sole polyol.

The two most widely used methods for incorporating polyols into alkyds are alcoholysis and direct esterification. Table 2 lists typical formulations and properties of the resulting resins for each of the four major classes of alkyds prepared.

Alcoholysis

The alcoholysis procedure for preparing alkyds consists of reacting a triglyceride oil with a polyol to form fatty acid esters of the polyol. Alkyd synthesis is then completed by reacting these alcoholysis products with polybasic anhydrides or diisocyanates. Alcoholysis of triglycerides with glycol glycosides was best accomplished with catalysts of the types represented by litharge and lithium hydroxide, the latter being pre-

Table 2—Typical Alkyd Formulations and Properties

Components	ALKYD TYPE					
	Short Oil		Medium Oil		Long Oil	Urethane
	RESIN NO.					
	348	372	330	343	324	205
	METHOD ^a					
A	D	A	D	A	A	
Weight, Grams						
Linseed oil	—	—	520.0	—	600.0	—
Soybean oil	403.4	—	—	—	—	—
Safflower oil	—	—	—	—	—	650.0
Soya fatty acid	—	—	—	491.0	—	—
Tall oil fatty acid	—	400.0	—	—	—	—
Phthalic anhydride ..	343.2	310.0	271.4	273.9	225.0	—
Maleic anhydride	9.9	27.0	9.1	25.8	6.0	—
Toluene diisocyanate	—	—	—	—	—	212.3
Glycol glycosides (dry basis)	131.0	128.6	130.6	116.0	101.0	109.0
Glycerol	151.7	193.2	102.4	158.9	84.0	25.8
Lithium hydroxide	0.2	—	0.3	—	0.3	0.3
Hypophosphorus acid	4.0	4.1	2.6	5.2	1.5	—
Dibutyl tin dilaurate	—	—	—	—	—	0.3
Anthraquinone	2.0	—	2.6	—	2.6	4.0
Properties						
Oil length	40	42	52	51	61	65
Viscosity, Stokes/sec ^b	40.5	23.0	—	41	18	21
Color, Gardner ^b	7	6	6	5	7	6
Acid value, 100% solid	11.4	11.4	6	12	8	—

(a) A = esterification by alcoholysis; D = direct esterification.

(b) At 50% solids for short and medium oils, 60% solids for urethanes, and 70% solids for long oils.

ferred. Preferred catalyst concentrations ranged from 0.01 to 0.15%, based on the dry weight of polyol. An alcoholysis temperature of 255 to 260 C was used, which permitted short reaction times. In general, the alcoholysis procedure was preferred for preparing long and medium length and urethane alkyds.

Typical cooking procedures for all alcoholysis formulations shown in *Table 2* are: mix the oil, glycol glycoside (30% water), anthraquinone, and enough xylene (about 6%) to give the desired reflux temperature then heat rapidly to 200 C with good stirring and a nitrogen blanket. At this temperature, add a mixture containing 25% of the glycerol and all the lithium hydroxide catalyst. Continue heating at 255 to 260 C and hold at this temperature until a methanol solubility of 3 to 1 is reached. Usually it takes about an hour to reach this level. Cool to 150 C and add the hypophosphorus acid, phthalic and maleic anhydrides, balance of glycerol, and enough xylene to give a reflux temperature of 175 to 180 C. Then heat at 175 to 180 C until the desired acid value and viscosity are reached. Finally, remove the xylene, adjust to 70% nonvolatiles for long oil alkyds and to 50% nonvolatiles for short and medium length alkyds with mineral spirits and filter.

Direct Esterification

In the direct esterification method a fatty acid replaces the triglyceride. About 1-2% (based on polyol) of hypophosphorus acid catalyst and a reaction temperature of 160 to 170 C are adequate for this method. The direct procedure was generally preferred for preparing short oil length alkyds.

Typical cooking procedures for all direct esterification formulations shown in *Table 2* are: mix the fatty acid, glycol glycoside (30% water), enough xylene to give the desired reflux temperature, and half of the hypophosphorus acid and then heat the mixture rapidly to 150 to 160 C with good stirring and a nitrogen blanket. When the mixture is free of water, add the phthalic anhydride and react at 160 to 170 C for 30 to 35 minutes. Then add the glycerol and remaining acid catalyst. Continue the heating at 175 to 180 C until an acid value of 30 to 35 is reached and add the maleic anhydride. When the desired acid value and viscosity are reached, remove the xylene and cool. Finally, dilute to 50% nonvolatiles with mineral spirits and filter.

Urethane Alkyds

Urethane alkyds were prepared by a two-step process. First, an oil was reacted with a polyol by the alcoholysis procedure to give intermediate products containing hydroxyl groups. Second, these hydroxyl-containing esters were cross-linked with toluene diisocyanate.

Typical cooking procedures for the formulation shown in *Table 2* are: mix the oil, glycol glycoside (30% water), anthraquinone, and xylene then heat rapidly to 255 to 260 C with good stirring and a nitrogen blanket. Then add the glycerol and lithium hydroxide catalyst. Continue heating at 255 to 260 C until methanol solubility is 2 to 1. Remove the xylene and cool to room temperature. Next, add the mineral spirits and heat to 60 C. At this temperature, add the toluene diisocyanate slowly and then heat to 100 C. Add the dibutyl tin dilaurate catalyst and hold at 100 C until a viscosity of 17 to 27 Stokes is reached. Finally, cool the reaction mixture and dilute to 60% nonvolatiles with methyl Cellosolve.[®]

ALKYD FILM AND ENAMEL EVALUATIONS

Short Oil Length Alkyds

Glycol glycosides show most promise in short-oil alkyds. These alkyds were prepared by both direct esterification and alcoholysis according to representative formulations reported in *Table 2*. Generally, the direct method gave short-oil alkyds with better drying properties.

For clear film evaluations (*Table 3*) mixtures containing 40% alkyd, 58.9% mineral spirits, 0.7% of a 24% lead naphthalate solution, and 0.4% of a 6% cobalt

Table 3—Short-Oil Alkyds: Clear Film Evaluation (Air Drying)

Properties	RESIN NUMBER					
	341	372	Control	346	348	Control
	METHOD ^a					
	D	D	D	A	A	A
	OIL LENGTH					
	40	42	Short	41	40	Short
	OIL OR FATTY ACID (FA)					
	Linseed FA	Tall Oil FA	—	Safflower	Soybean	—
	ANHYDRIDE ^b					
	PA+MA	PA+MA	—	PA+MA	PA+MA	—
Speed of drying						
Finger transfer, hour	1.0	1.0	—	0.75	0.75	—
200 grams Zapon, hour	2.0	2.0	—	7.0	8+	—
500 grams Zapon, hour	2.5	2.5	5.5	7.0	8+	5.5
Hardness						
Sward, 24 hours	26	14	26	20	14	30
1 week	34	22	28	28	24	36
2 weeks	32	20	—	26	24	—
Tukon, 1 week	5.98	1.66	3.64	2.59	2.31	3.01
2 weeks	6.45	1.69	—	3.21	2.21	—
Flexibility						
G.E., direct/reverse	20/60	20/60	—	20/20	2/5	—
1/8-inch Mandrel bend	Pass	Pass	Pass	Pass	Pass	Pass
Yellowing "b" value						
Initial	4.6	4.3	4.3	4.3	4.4	4.3
After 5 hours, 180 F (82 C)	7.2	5.4	5.9	5.8	5.5	5.7

(a) A = esterification by alcoholysis; D = direct esterification.

(b) PA+MA = Phthalic plus maleic anhydride.

naphthalate were stored for 24 hours and then drawn to 1.5-mil thickness on tin and glass plates. Because short-oil alkyds have a low percentage of oil and subsequently fewer double bonds for cross-linking, they are generally not used in air-dry applications. Instead, they are used as baking vehicles either alone or in combination with amino resins. Glycol glycoside-based alkyds, prepared by alcoholysis, are slow drying (Table 3) and, consequently, not considered acceptable for air-dry applications. However, the short-oil alkyds, prepared by direct esterification, show surprisingly good properties for air-dry use. Their finger transfer time of one hour and 500-gram Zapon of 2.5 hours illustrate practical dry times. Furthermore, they develop good hardness in 24 hours. These films also show acceptable solvent and chemical resistances and flexibility.

Since these short-oil resins showed promise for industrial applications they were evaluated more extensively. First, they were formulated with 15% melamine, cast, and baked. Data in Table 4 reveal that the glycoside-based resins prepared by both alcoholysis and direct esterification perform as well as a control based on pentaerythritol-glycerol-tall oil fatty acids. However, they yellow somewhat more rapidly than the control.

Next, the short-oil alkyds were formulated, by standard procedures, into white enamels for both air-dry and bake-dry evaluations. To make these paints,

Table 4—Short-Oil Alkyds with 15% Melamine: Baked Clear-Film Evaluation

Properties	RESIN NUMBER		
	372	346	Control
	METHOD ^a		
	D	A	D
	OIL OR FATTY ACID (FA)		
	Tall Oil	Tall Oil	Tall Oil
	FA	Safflower	FA
Hardness			
Sward, 15 minutes at 300 F (149 C)	30	30	30
Tukon, 15 minutes at 300 F	4.06	7.36	4.53
Hot tack	SL ^b	N	SL
Yellowing "b" value			
15 Minutes at 300 F	5.3	6.0	4.8
18 Hours at 300 F	16.1	22.6	12.6
Flexibility			
G. E., direct/reverse	60/60	60/60	60/60
1/8-inch Mandrel bend	Pass	Pass	Pass
Solvent resistance			
Water	S	S	S
HCl, 10%	NE	NE	NE
NaOH, 3%	S	S	S
Xylene	S	S	S
Mineral spirits	NE	NE	NE

(a) A = esterification by alcoholysis; D = direct esterification.

(b) SL, slight tack; N, no tack; S, softens; SS, slight softening; NE, no effect.

**Table 5—Short-Oil Alkyds:
Evaluation in Bake-Dry White Enamels**

Properties	RESIN NUMBER		
	348	372	Control
Hot tack, 30 minutes at 250 F ^a (121 C)	SL	N	SL
Hardness, pencil	HB	B	HB
Flexibility			
G. E., direct/reverse	60/60	60/60	60/60
1/8-inch Mandrel bend	Pass	Pass	Pass
Gloss, 60°			
Initial	75	87	80
24 hours in humidity chest ^b	66	83	80
72 hours in humidity chest	72	33	74
212 hours in humidity chest	46	20	45
Salt fog, 5% 48 hours rust creep, ^c inches	2/32	6/32	4/32
Initial gloss, 60°/20°	82/64	88/71	84/59
Overbake, 16 hours at 300 F			
Gloss, 60°/20°	74/37	73/33	81/51
"b" Value	12.6	12.8	11.1

(a) SL, slight tack; N, no tack.

(b) Federal Test Method, No. 141, Method 6201.

(c) Federal Test Method, No. 141, Method 6061.

the resin, pigment (TiO₂), and solvent were mixed and ground on a pebble mill for 16 hours to achieve complete dispersion. After this initial grinding, more resin was added along with driers according to the type of dry application desired. Solvent was then added to give the proper application viscosity. The paints were then drawn into 1.5-mil films on glass and tin plates and evaluated (Tables 5 and 6).

Resins 348 and 372 were each formulated into bake-dry white enamels and compared to a control

formulated with trimethylolpropane-glycerol soya oil based short-oil (Table 5). Both experimental resins performed well in comparison to the control. However, the tall oil fatty acid resin, No. 372, gave inferior resistance to 72- and 212-hour humidity tests.

Although short-oil alkyds are not generally used for air-dry applications, unless specifically formulated for this purpose, these experimental resins show excellent performance in this application (Table 6). Those formulated with safflower oil (No. 346) and tall oil fatty acid (No. 372) were superior to the control in speed of drying, flexibility, and initial "b" value (yellowing). They were inferior only in the aged "b" value.

Medium Oil Length Alkyds

A variety of medium oil length alkyds were prepared from soybean, linseed, and safflower fatty acids and oils employing glycol glycoside in combination with glycerol as the polyol according to representative formulations shown in Table 2. Both alcoholysis and direct esterification procedures yielded acceptable alkyds; however, the alcoholysis procedure was deemed more desirable for synthesis of medium-oil resins.

For clear film evaluations (Table 7), mixtures containing 40% alkyd, 59.1% mineral spirit, 0.6% of a 24% lead naphthalate, and 0.3% of a 6% cobalt naphthalate were stored for 24 hours and then drawn to 1.5-mils thickness on tin and glass plates. Generally the medium oil length alkyds based on glycol gly-

Table 6—Short- and Medium-Oil Alkyds: Evaluation in Air-Dry White Enamels

Properties	RESIN NUMBER						
	Short Oils			Medium Oils			
	346	372	Control	330	331	343	Control
	METHOD ^a						
	A	D	—	A	A	D	—
OIL OR FATTY ACID (FA)							
	Safflower	Tall Oil FA	—	Linseed	Safflower	Soya FA	—
Speed of drying							
Set to touch, minute	5	5	5	23	22	18	38
200 grams Zapon, hour	3.6	5.8	8+	4.5	5.5	8+	5.0
500 grams Zapon, hour	3.6	6.0	8+	4.5	5.5	8+	6.5
Hardness							
Sward, 24 hours	—	—	—	24	20	12	14
Pencil, 2 weeks	2B	2B	2B	2B	2B	3B	3B
Flexibility							
G. E., direct/reverse, 2 weeks	20/5	40/40	2/10	20/40	20/40	60/60	60/60
1/8-inch Mandrel bend, 2 weeks	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Initial							
Gloss, 60°/20°	93/84	91/81	93/87	89/82	85/72	94/88	91/84
"b" value	0.1	0.3	0.7	0.5	0.2	0.1	0.1
Reflectance	84	86	85	86	86	84	85
After 5 hours, 180 F (82 C)							
Gloss, 60°/20°	88/66	87/71	91/83	84/61	73/37	85/65	86/70
"b" value	2.5	0.7	0.2	3.9	3.5	2.7	3.7
Reflectance	84	85	84	85	85	84	84
Sag test rating	—	—	—	5	6	5	5
Leveling value	—	—	—	5+	9—	5+	6—
Brushability	—	—	—	Good	Good	Good	Good

(a) A = esterification by alcoholysis; D = esterification by the direct method.

Table 7—Medium-Oil Alkyds: Clear Film Evaluation

Properties	RESIN NUMBER						
	129	330	Control	309	343	345	Control
	METHOD ^a						
	A	A	A	D	D	D	D
	OIL LENGTH						
	54	52	Medium	54	51	50	Medium
	OIL OR FATTY ACID (FA)						
	Linseed	Linseed	Linseed	Tall Oil FA	Soya FA	Linseed FA	Soya FA
	ANHYDRIDE ^b						
	THPA	PA+MA	—	PA+MA	PA+MA	PA+MA	—
Speed of drying							
Finger transfer, minute	45	45	45	55	55	40	40
200 grams Zapon, hour	2.0	2.0	—	7.5	1.1	2.0	4.0
500 grams Zapon, hour	2.0	2.0	6.0	8.0	1.3	1.3	6.0
Hardness							
Sward, 24 hours	30	22	10	12	16	20	12
1 week	48	36	24	20	22	28	18
2 weeks	58	34	—	20	20	26	16
Tukon, 1 week	7.3	3.9	Soft	1.74	2.07	2.69	1.58
2 weeks	7.0	3.3	—	1.8	2.04	3.20	1.69
Flexibility							
G. E., direct/reverse	—	40/60	—	60/60	60/60	60/60	60/60
1/8-inch Mandrel bend	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Yellowing "b" value							
Initial	—	4.9	4.9	4.3	4.3	4.5	4.4
After 5 hours, 180 F	—	7.7	7.5	5.5	5.9	7.2	6.5

(a) A = esterification by alcoholysis; D = esterification by direct method.

(b) TPHA = tetrahydrophthalic anhydride; PA+MA = phthalic plus maleic anhydride.

coside-glycerol combinations yielded clear films that were equal, or superior, to controls based on sorbitol-glycerol combinations. The experimental alkyds showed good fast drying and hardness properties which would place them in maintenance enamels, porch, deck and trim paints, and machine and implement enamels. The 24-hour Sward hardness values of 12 to 30 suggest that the alkyds would have excellent scuff resistance for the applications listed. Yellowing properties are quite acceptable—as expected, soybean alkyds are better than linseed alkyds.

Although the practical application of alkyds based on tetrahydrophthalic anhydride is somewhat limited, one resin (No. 129) based on this anhydride is reported. The resin showed exceptionally high Sward and Tukon hardness. However, such films are more brittle than those based on phthalic anhydride.

The medium-oil alkyds were further evaluated in air-dry white enamel formulations (Table 6). They showed practical drying rates that could allow their use for both interior and exterior applications. All formulations tested would allow for overnight dry and recoat. Surface and aged hardness were acceptable. Sag test rating, leveling values, and brushability of the enamels were quite acceptable for commercial applications.

Long Oil Length Alkyds

Linseed, safflower, and soybean long oil length alkyds were prepared from glycol glycoside-glycerol

combinations according to the alcoholysis formulation shown in Table 2. Acceptable long-oil alkyds were not obtained by the direct esterification procedure.

For clear film evaluations (Table 8), mixtures containing 55% alkyd, 43.5% mineral spirit, 1% of a 24% lead naphthalate solution, and 0.5% of a 6% cobalt naphthalate solution were stored for 24 hours and then drawn to 1.5-mil thickness on tin and glass plates. Glycol glycoside-based alkyds formulated with tetrahydrophthalic anhydride (Nos. 55 and 107) produced films that were outstanding in all properties measured; however, they performed poorly on exposure tests. Severe chalking was also encountered. Those formulated with phthalic anhydride were comparable to films cast from controls formulated with pentaerythritol-glycerol combinations. All alkyds had good overnight drying which would allow for a 24-hour recoat application—a very important characteristic for trade sale alkyds. In addition to properties shown in Table 8, the experimental films compared well with the controls in respect to solvent and chemical resistances.

Three long-oil resins based on linseed, safflower, and soya oils and formulated as shown for resin 324 (Table 2) were used to prepare pigmented white enamels for two years of Florida exposure. Only six months of the program has been completed. During these first months the experimental enamels were judged equal to commercial controls in mold resistance, chalking characteristics, and general appear-

Table 8—Long-Oil Length Alkyds: Clear Film Evaluation

Properties	RESIN NUMBER					
	55	107	324	325	Control	Control
	OIL LENGTH					
	58	70	61	61	Long	Long
	OIL					
	Linseed	Linseed	Linseed	Safflower	Linseed	Safflower
	ANHYDRIDE ^a					
	THPA	THPA	PA+MA	PA+MA	PA+MA	PA+MA
Speed of drying						
Finger transfer, hour	1.0	1.3	2.0	2.7	2.0	1.5
200 grams Zapon, hour	3.5	3.0	2.5	2.7	—	—
500 grams Zapon, hour	4.5	3.5	4.0	4.0	4.0	3.0
Hardness						
Sward, 24 hours	12	18	12	10	14	14
1 week	48	28	16	12	20	18
2 weeks	50	30	20	12	—	—
Tukon, 1 week	4.74	1.68	1.31	0.83	0.80	0.90
2 weeks	8.37	1.96	1.21	0.93	—	—
Flexibility						
G. E., direct/reverse	60/60	—	60/60	60/60	—	—
1/8-inch Mandrel bend	Pass	Pass	Pass	Pass	Pass	Pass
Yellowing "b" value						
Initial	—	—	5.3	4.8	4.9	4.6
After 5 hours, 180 F	—	—	9.4	7.1	8.4	6.9

(a) THPA = tetrahydrophthalic anhydride; PA+MA = phthalic plus maleic anhydride.

ance. They were rated slightly inferior in retention of 60° gloss.

Urethane Alkyds

Clear film evaluations (Table 9) reveal that the glycol glycoside-glycerol urethane alkyds have excellent properties when compared with a standard control based on pentaerythritol-glycerol. The experimental resins were superior in abrasion resistance, equal or slightly superior in all other tests except initial gloss. Initial 60°/20° angle gloss was lower than the control; however, after 65 hours of exposure, the difference in gloss retention became negligible. As expected, the urethane films yellow more rapidly than anhydride-based alkyds, but in this regard the experimental resins were rated equivalent to the control.

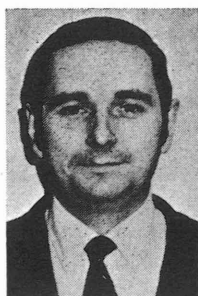
SUMMARY AND CONCLUSIONS

Glycol glycosides were successfully prepared in large scale quantities and were estimated to have a potential selling price about half those of polyols now used in alkyds. Reaction conditions were established for incorporating the glycosides into four major classes of alkyds. The glycosides can replace only about 55% of the polyol system. This restriction is apparently due to dehydration, steric hindrance, and low solubility of the glycosides. The glycosides are heat sensitive at conventional alkyd reaction temperatures, as are other carbohydrate derivatives; consequently, special precautions such as the use of inert gas blankets, rapid stirring, and efficient reaction conditions must be maintained during alkyd preparations. When these

Table 9—Urethane Alkyds: Clear Film Evaluations

Properties	RESIN NUMBER		
	205	198	Control
	OIL		
	Safflower	Linseed	Safflower
Speed of drying			
Finger transfer, minute	40	40	40
200 grams Zapon, hour	1.7	1.7	1.7
500 grams Zapon, hour	3.1	1.7	1.8
Hardness			
Sward, 6 hours	16	16	16
24 hours	24	24	22
1 week	36	44	34
2 weeks	36	44	34
Tukon, 24 hours	2.82	2.61	2.22
1 week	4.30	5.09	3.52
2 weeks	4.28	5.69	3.35
Yellowing "b" value			
After 2 weeks	5.6	6.2	5.9
After 5 hours at 180 F	11.4	12.7	10.8
Flexibility after 2 weeks			
G. E., direct/reverse	60/60	60/60	60/60
1/8-inch Mandrel bend	Pass	Pass	Pass
Abrasion resistance after			
2 weeks aging ^a	38	50	53
Gloss, 60°/20°, on wood			
Initial	69/25	70/26	80/26
65 hours	61/16	64/14	61/12
109 hours	58/16	60/12	55/10
155 hours	47/8	41/6	23/8
207 hours	28/3	29/4	23/2
251 hours	20/2	19/3	18/2
304 hours	8/1.4	8/1.4	8/1.4
Gloss, 60°/20°, on paper			
Initial	84/38	88/45	92/65
65 hours	57/22	58/21	56/22
109 hours	27/4	29/4	26/4
155 hours	20/3	27/3	25/3

(a) Milligram film loss/1000 revolutions.



Dr. William J. McKillip is Group Leader of the Ashland Chemical Basic Research being conducted at the Minneapolis Research facility. His research interests include the design of new polymers. Dr. McKillip has written several papers on the preparation and utilization of aminimides, a new reactive group for polymer utility. He received his B.S. Degree from Loras College, Dubuque, Iowa and his Ph.D. Degree in Organic Chemistry at the University of Iowa.

Clarence N. Impola joined the former Archer-Daniels-Midland Chemical Division, now part of the Ashland Chemical Co., in 1957 as a chemist. He received a B.S. Degree from the University of Minnesota, Duluth, Minn. Mr. Impola has been involved in a number of government sponsored projects utilizing chemicals derived from starch. His major interest lies in product development and application.



James N. Kellen, chemist at the Ashland Chemical Research Laboratory, joined the Corporate Research Group in 1966 after earning his B.S. Degree in Chemistry from St. John's College, Collegeville, Minn. Mr. Kellen's responsibilities have involved synthesis of chemical intermediates for new products. Mr. Kellen is currently working toward a Ph.D. Degree in Organic Chemistry at the University of Iowa, Iowa City.

Robert W. Buckney, chemist at the Ashland Chemical Research Laboratory since 1966, earned his B.S. Degree in Biology from Iowa Wesleyan College in 1950. Mr. Buckney's interests are in product application areas, specifically coatings evaluation.



Felix H. Otey, chemist at the Northern Regional Research Laboratory since 1956, earned his B.S. Degree in Chemistry from Murray State College in 1948 and a master's degree from the University of Missouri in 1950. His work at the Peoria Laboratory has dealt with the development of new industrial uses for starch as raw material in surfactants, coatings, and urethane foams.

precautions are observed, alkyds with commercially acceptable color, viscosity, and acid number can be made. The direct esterification method generally gave resins with the best color and drying characteristics.

The alkyds in both clear and pigmented films were generally superior in drying and hardness, equal in flexibility, and slightly inferior in gloss and yellowing characteristics when compared with commercial controls.

The experimental short-oil resins have properties desirable for both air-drying and bake-drying applications. They could be used as vehicles in appliance finishes such as cabinets, furniture, refrigerators, in maintenance enamels, antirust primers, or any of the various coatings where industrial short-oil resins are now used. The glycoside-based medium oils have acceptable colors, drying rates, hardness, and flexibility that would allow their use as vehicles in industrial finish enamels for farm implements, railroad cars, hardware, metal furniture, primers, automotive refinishing, and a variety of other typical medium-oil applications. Long-oil resins based on glycol glycosides have acceptable clear film properties for industrial applications. Furthermore, exterior studies being made in Florida have shown that at the end of 6 months the pigmented long-oil resins are comparable to selected commercial resins based on glycerol and other polyol combinations. The new urethane alkyds followed the expected pattern for this class of resins in that they were fast drying, hard, tough, and highly resistant to abrasion and chemicals.

Because of the great variety of formulating techniques available for exploring the potential utility of a new polyol in alkyd applications, it was impractical to investigate each area in detail. Experiments could have been designed to cover a much wider range of conditions and formulations which would possibly have produced resins with improved properties. However, these experiments were sufficient to show that alkyds meeting commercial standards can be produced from glycol glycosides.

ACKNOWLEDGMENT

The authors wish to thank Owen Paukner, of the Ashland Chemical Resin Division, for his guidance and assistance during the course of this work. ♦

References

- (1) Synthetic Organic Chemicals, U. S. Production and Sales, 1966, T. C. Publication 248, U. S. Gov. Printing Office, Washington, D. C.
- (2) Otey, F. H., Bennett, F. L., Zagoren, B. L., and Mehlretter, C. L., *Ind. Eng. Chem. Prod. Res. Develop.*, 4, 228 (1965).
- (3) Otey, F. H., Mehlretter, C. L., and Rist, C. E., *J. Am. Oil Chem. Soc.*, 40, 76 (1963).
- (4) Otey, F. H., Zagoren, B. L., and Mehlretter, C. L., *Ind. Eng. Chem. Prod. Res. Develop.*, 2, 256 (1963).
- (5) Leitheiser, R. H., Impola, C. N., Reid, R. J. and Otey, F. H., *Ind. Eng. Chem. Prod. Res. Develop.*, 5, 276 (1966).
- (6) Otey, F. H., Mehlretter, C. L. and Rist, C. E., *Cereal Sci. Today*, 13, 199 (1968).